

Quantum Measurement Theory Explains the Deuteration Effect in Radical-Ion-Pair Reactions

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It has been recently shown that radical-ion pairs and their reactions are a paradigm biological system manifesting non-trivial quantum effects, so far invisible due to the phenomenological description of radical-ion-pair reactions used until now. We here use the quantum-mechanically consistent master equation describing magnetic-sensitive radical-ion-pair reactions to explain experimental data [C. R. Timmel and K. B. Henbest, *Phil. Trans. R. Soc. Lond. A* **362**, 2573 (2004); C. T. Rodgers, S. A. Norman, K. B. Henbest, C. R. Timmel and P. J. Hore, *J. Am. Chem. Soc.* **129** 6746 (2007)] on the effect of deuteration on the reaction yields. Anomalous behavior of radical-ion-pair reactions after deuteration, i.e. data inconsistent with the predictions of the phenomenological theory used so far, has been observed since the 70's and has remained unexplained until now.

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The possible existence of non-trivial quantum effects in biology [1] has fueled a tumultuous and ongoing debate [2], as on the one hand effects associated with quantum coherence are generally understood to be suppressed in the typical biological/biochemical environment, on the other hand, it is rightly assumed that nature must have found a way to utilize the operational advantages offered by quantum physics, in particular quantum coherence[3, 4] and quantum entanglement.

It has been recently shown [5] that a familiar biological system, namely radical-ion pairs and their reactions, exhibits the full spectrum of non-trivial quantum effects familiar from quantum information science, namely quantum coherence, quantum jumps, the quantum Zeno effect, and in principle quantum entanglement. Radical-ion pairs play a fundamental role in a series of biologically relevant chemical reactions, ranging from charge transfer initiated reactions in photosynthetic reaction centers [6] to magnetic sensitive reactions abounding in the field of spin-chemistry [7], and in particular in the biochemical processes understood to underlie the biological magnetic compass of several species having the ability to navigate in earth's magnetic field [8, 9].

In Fig. 1 we depict a generic model for radical-ion-pair reactions. Photoexcitation of a donor-acceptor molecule DA followed by charge-transfer creates a radical-ion-pair with the two unpaired electrons in the singlet state $(D^+A^-)^S$. Magnetic interactions induced by the external magnetic field and the internal hyperfine couplings of the unpaired electrons with the molecule's nuclear spins bring about a coherent mixing of $(D^+A^-)^S$ with $(D^+A^-)^T$, the triplet radical-ion-pair. Both singlet and triplet radical-ion pairs charge-recombine with rates k_S and k_T to singlet and triplet products, respectively. This reaction forms a magnetic sensor since the product yields depend on the external magnetic field. However, radical-ion-pair reactions have so far been described (see e.g. re-

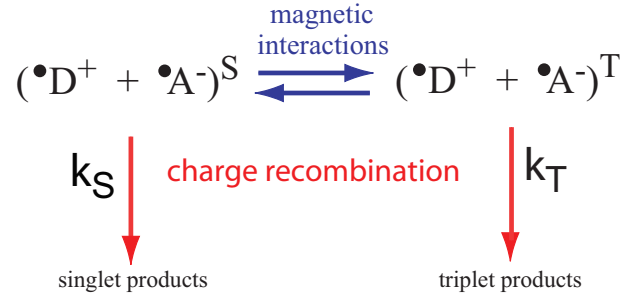


FIG. 1: Radical-ion-pair reaction dynamics: magnetic interactions within the donor-acceptor molecule are responsible for the singlet-triplet coherent mixing, while charge recombination into singlet and triplet products, with respective rates k_S and k_T removes molecular population from the singlet-triplet subspace.

view [10]) with a phenomenological density matrix equation that (a) has by design not allowed the true quantum nature of these reactions to be unveiled, and (b) has led to several inconsistencies between theory and experiment. We have recently put forward [5] the correct quantum dynamic description of radical-ion-pair reactions following from quantum measurement theory. In fact, there is a very similar system familiar in condensed matter physics, namely coupled quantum dots, that is treated with the same formalism, as described among others, in the works of Milburn, Wiseman and co-workers [11]. We will here use this quantum-mechanically consistent formalism to account for quite a severe disagreement between experiments and the phenomenological theory that has to do with deuteration. We will first fully reproduce reaction data of the radical-ion-pair Pyrene-Dymethylaniline (PyDMA) and its deuterated versions, while we also show that the phenomenological theory fails to account for the same data. We will then use a simple theoretical model of a radical-ion-pair to explain why the observed effects

are fundamentally different from what one would expect from the phenomenological dynamics which in some cases is rather intuitive. Using this simple model we will finally account for an older observation of this "anomalous" effects of deuteration dating to 1979.

For completeness, we here reiterate the phenomenological as well as the new master equation describing the spin state evolution of the radical-ion-pair. The spin Hilbert space of every radical-ion-pair consists of the two unpaired electron spins and any number of nuclear spins. This spin system is an open quantum system due the reservoir states inducing charge recombination. The master equation describes both the unitary evolution of the spin state due to magnetic interactions as well as the measurement evolution due to the reservoir states (vibrational excited states of the neutral recombined molecule). Until now the spin state evolution of a radical-ion-pair has been described with the phenomenological master equation

$$d\rho/dt = -i[\mathcal{H}, \rho] - k_S(Q_S\rho + \rho Q_S) - k_T(Q_T\rho + \rho Q_T) \quad (1)$$

where Q_S and Q_T are the singlet and triplet state projection operators, respectively. The first term in (1) is the unitary evolution due to the magnetic interactions, while the second and third terms attempt to take into account population loss out of the radical-ion-pair Hilbert subspace due to charge recombination. It is these terms that are phenomenological and that suppress by force the existing quantum-mechanical effects like the quantum Zeno effect [12]. On the other hand, the actual quantum dynamic evolution of the radical-ion-pair spin density matrix ρ is given by the equations

$$d\rho/dt = -i[\mathcal{H}, \rho] - (k_S + k_T)(Q_S\rho + \rho Q_S - 2Q_S\rho Q_S) \quad (2)$$

where the second term describes the measurement-induced evolution brought about by the singlet (rate k_S) and triplet (rate k_T) recombination channel. Due to the completeness relation $Q_S + Q_T = 1$, both channels effectively "measure" the observable Q_S with a total measurement rate $k_S + k_T$. The unconditional evolution described by (2) is interrupted by the charge-recombining quantum jumps described by equations (3) which give the probability of the singlet and triplet recombination taking place within the time interval between t and $t+dt$, i.e.

$$\begin{aligned} dP_S &= 2k_S\langle Q_S \rangle dt \\ dP_T &= 2k_T\langle Q_T \rangle dt, \end{aligned} \quad (3)$$

The density matrix ρ describing the spin state of the two unpaired electrons and n nuclear spins has dimension $d = 4 \prod_{j=1}^n (2I_j + 1)$, where I_j is the nuclear spin of nucleus j . Coming to the magnetic Hamiltonian \mathcal{H} , it is composed of \mathcal{H}_Z , the Zeeman interaction of the two unpaired electrons (nuclear Zeeman interaction is negligible) with the external magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$, \mathcal{H}_{hf} , the

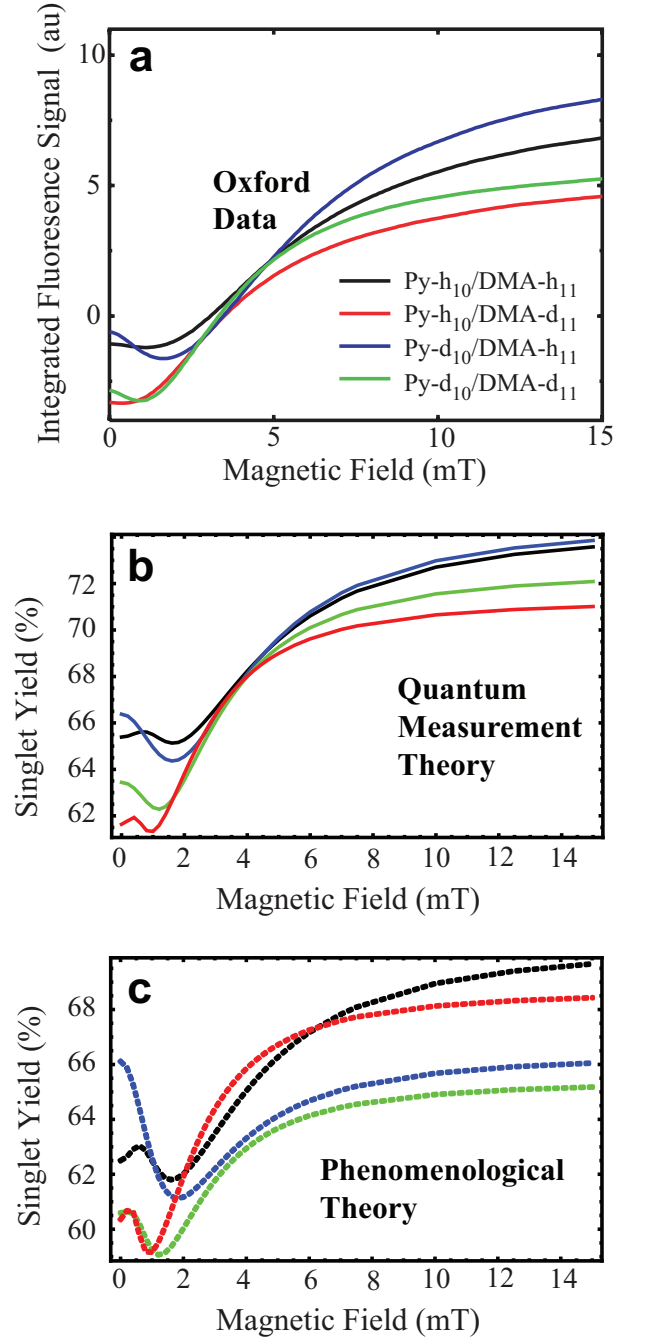


FIG. 2: (a) Experimental data from [7, 13]. (b) Reproduction of the data with quantum measurement theory equations (2) and (3). (c) Failure of phenomenological theory (1) to reproduce data.

hyperfine couplings of the electrons with the surrounding nuclear spins

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{\text{hf}}, \quad (4)$$

with $\mathcal{H}_Z = \omega(s_{1z} + s_{2z})$, $\mathcal{H}_{\text{hf}} = \sum_{i=1}^2 \sum_{j=1}^n \mathbf{s}_i \cdot \mathbf{A}_{ij} \cdot \mathbf{I}_j$, where the sum over i is for the two electrons and the sum over j for the n nuclear spins, with \mathbf{A}_{ij} the hyperfine

TABLE I: Hyperfine Couplings and Recombination Rates for the Data Reproduction

	A_{Py} (mT)	A_{DMA} (mT)	k_S (μs^{-1})	k_T (μs^{-1})
Py-h ₁₀ DMA-h ₁₁	1.9	6.7	8.5	4.0
Py-d ₁₀ DMA-h ₁₁	0.4	5.0	12.0	11.4
Py-d ₁₀ DMA-d ₁₁	0.9	4.2	7.9	6.0
Py-h ₁₀ DMA-d ₁₁	1.3	4.0	3.7	1.8

coupling tensor of electron i with nuclear spin j .

We will now reproduce recent experimental data by Hore and co-workers [7, 13] on the reaction of the radical-ion-pair Py-DMA and its deuterated versions. In the reproduction of the experimental data we will use a simple radical-ion-pair model consisting of just two spin-1/2 nuclei. In Figure 2a we depict the fluorescence measurement of the Py-DMA reaction and its deuterated versions. In Figure 2b we reproduced the data with the hyperfine couplings shown in Table 1, while for the same parameters, the prediction of the phenomenological theory (1) is shown in Figure 2c. The agreement of the former and the severe discrepancy of the latter with the data is rather obvious.

Finally we will resolve an old problem regarding deuteration that clearly illustrates the qualitative understanding of radical-ion-pair reactions that the phenomenological description fails to embody. To illustrate the problem we use the simplest possible radical-ion-pair model, that with just one spin-1/2 nucleus. We calculate according to both quantum measurement theory (2) and (3) and phenomenological theory (1) the triplet yield of the reaction as a function of the isotropic hyperfine coupling A , i.e. the magnetic Hamiltonian used for this calculations is just $\mathcal{H} = \omega(s_{1z} + s_{2z}) + As_1 \cdot \mathbf{I}$, with $I = 1/2$. The result is shown in Figure 3. It is readily seen that the triplet yield stays roughly constant according to the quantum measurement theory prediction, whereas it changes in a measurable way (a few %) according to the phenomenological description. In fact, the latter prediction is more intuitive, since it is based on the following plausible description: In the case when the singlet recombination rate is much larger than the triplet recombination rate, as in this particular example we are considering, the triplet yield should be proportional to the hyperfine coupling A , as the probability to recombine through the triplet channel should roughly scale as A/k_S , i.e. the singlet-triplet mixing rate A times the lifetime of the pair, $1/k_S$.

In Figure 4a we plot the evolution of the singlet projection operator expectation value, $\langle Q_S \rangle$, as calculated from the phenomenological density matrix equation (1), for two values of A , the hyperfine coupling. In contrast, the predictions of quantum measurement dynamics (2)

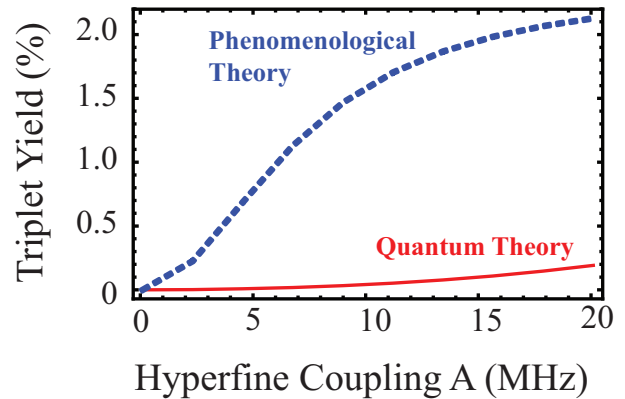


FIG. 3: Triplet yield of a one-nucleus (spin-1/2) radical-ion-pair as a function of the isotropic hyperfine coupling as calculated based on the quantum theory (red continuous line) and the phenomenological theory (blue dashed line). The calculation was done for an external magnetic field of 0.5 g and the singlet and triplet recombination rates were $k_S = 20 \mu s^{-1}$ and $k_T = 0.5 \mu s^{-1}$, respectively.

and (3) for these two different values of A are shown in Figure 4b and 4c, together with the corresponding unitary evolution (no recombination at all).

It is evident that for the same change in the hyperfine coupling, the relative change in $\langle Q_S \rangle$ is in reality (quantum measurement theory) larger than predicted by the phenomenological theory. However, due to the artificial structure of the latter (the phenomenological recombination terms) the absolute value of $\langle Q_S \rangle$ changes substantially during the reaction. In contrast, the actual change of $\langle Q_S \rangle$ is in reality much smaller exactly due to the projective nature of the recombination process that is embodied in the fundamental master equation (2). Thus the triplet reaction yield is in reality much less sensitive to the hyperfine coupling as naively and intuitively expected from the phenomenological understanding of the reaction. In other words, the phenomenological master equation (1) cannot account for the projective nature of the spin-conserving recombination channels, since it just describes a continuous disappearance of radical-ion-pairs due to the charge recombination process. On the contrary, as has been explained in [5], the fundamental master equation (2) takes into account the actual physical process that is going on: the recombination channels constitute a continuous measurement of the radical-pair's spin state, and as such, the latter is significantly affected.

The discrepancy that is visualized in Figure 3 is what Blankenship and Parson observed in 1979 with the P870-I radical-ion-pair and its deuterated version. It is noted that deuteration is effectively equivalent to a change in the relevant hyperfine couplings [14]. In fact, due to this severe inconsistency, these authors went as far as to doubt the validity of the basic singlet-triplet hyperfine mixing mechanism: "The identical triplet quantum yields in H

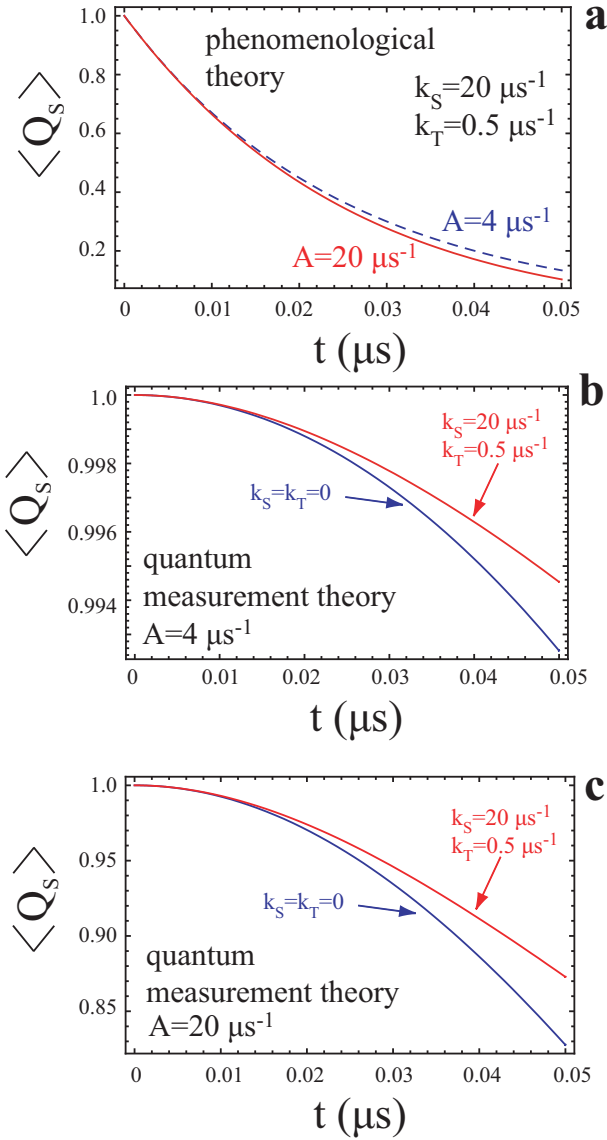


FIG. 4: (a) Evolution of $\langle Q_S \rangle$ based on the phenomenological theory for a time scale on the order of the duration of the reaction, $1/k_S = 0.05 \mu\text{s}$ and for two different values of the hyperfine coupling A (b) Evolution of $\langle Q_S \rangle$ based on quantum measurement theory with and without the recombination terms, for $A = 4 \mu\text{s}^{-1}$. (c) Evolution of $\langle Q_S \rangle$ based on quantum measurement theory with and without the recombination terms, for $A = 20 \mu\text{s}^{-1}$.

and D samples does not support the generally accepted

idea that hyperfine interactions are responsible for spin rephasing in the P870 I radical pair". Mention of this problem has also been made in the review [6].

In summary, we have shown that the quantum measurement dynamics present in radical-ion-pair reactions firstly explain recent experimental data and secondly resolve a long-standing discrepancy between the phenomenological description of these reactions that has been used until now and experimental observations. Radical-ion pairs and their reactions represent the first biological system where fundamental concepts of quantum mechanics and quantum information theory are fruitfully applied. The biological significance, if any, of this fact is a rather exciting question that surfaces from the above described change in our fundamental understanding of radical-ion-pair reactions.

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- [1] P. C. W. Davies, *Biosystems* **78**, 69 (2004).
- [2] D. Abbott *et al.*, *Fluctuations and Noise Letters* **8**, C5 (2008).
- [3] G. S. Engel *et al.*, *Nature* **446**, 782 (2007).
- [4] H. Lee, Y. C. Cheng and G. R. Fleming, *Science* **316**, 1462 (2007).
- [5] I. K. Kominis, arXiv:0806.0739.
- [6] S. G. Boxer, C. E. D. Chidsey and M. G. Roelofs, *Ann. Rev. Phys. Chem.* **34**, 389 (1983).
- [7] C. R. Timmel and K. B. Henbest, *Phil. Trans. R. Soc. Lond. A* **362**, 2573 (2004).
- [8] K. Schulten, *Adv. Solid State Phys.* **22**, 61 (1982).
- [9] T. Ritz, P. Thalau, J. B. Phillips, R. Wiltchko and W. Wiltchko, *Nature* **429**, 177 (2004).
- [10] U. Steiner and T. Ulrich, *Chem. Rev.* **89**, 51 (1989).
- [11] H. B. Sun and G. J. Milburn, *Phys. Rev. B* **59**, 10748 (1999); H. M. Wiseman *et al.*, *Phys. Rev. B* **63**, 235308 (2001); H.-S. Goan, G. J. Milburn, H. M. Wiseman and H. B. Sun, *Phys. Rev. B* **63**, 125326 (2001).
- [12] B. Misra and E. C. G. Sudarshan, *J. Math. Phys.* **18**, 756 (1977); W. M. Itano *et al.*, *Phys. Rev. A* **41**, 2295 (1990); P. Facchi and S. Pascazio, *Fortschr. Phys.* **49**, 941 (2001); K. Koshino and A. Shimizu, *Phys. Rep.* **412**, 191 (2005); A. G. Kofman and G. Kurizki, *Nature* **405**, 546 (2000).
- [13] C. T. Rodgers, S. A. Norman, K. B. Henbest, C. R. Timmel and P. J. Hore, *J. Am. Chem. Soc.* **129**, 6746 (2007).
- [14] R. E. Blankenship and W. W. Parson, *Biophys. J.* **25**, 205a (1979).